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660266

No. 660.266

International Classification
Patent presented on:
8-25-1965

MINISTRY OF ECONOMIC AFFAIRS
PATENT

Ministry of Economic Affairs (*Illegible*)
Having taken into consideration the Patent Law dated May, 1854:

Considering the official report drawn up on February 25, 1965 at 3:50 PM
at the Patent Rights Service;
ORDER:

Article 1. - Was delivered to the company known as: STAUFFER CHEMICAL COMPANY, 380 Madison Avenue, New York, N. Y. (United States of America) represented by Bureaux Vander Haeghen in Brussels,

a patent on an invention for: New herbicidal compounds and their use.
which states to have been the subject of a patent application, not yet granted to date, filed in the United States of America on September 13, 1963 in the name of Misters D.R. Baker, S. Y.C. Soong and B.H. Lake who claim to own the rights to this patent.

Article 2. — This patent has been delivered without prior examination, with its risks and perils, with no guarantee of the innovation or the merit of the invention or of the exactness of its description, and without prejudice to the rights of third parties.

With the present decree, the duplicates of the specifications of the invention shall remain as joint, (memory description and possibly drawings) and signed by the interested party and filed in support of the patent application.

Brussels, August 25, 1965
BY SPECIAL DELEGATION:
The Director General,
J. HAMELS

R-318
B.38.946
TO

660266

DESCRIPTION

joint & single application for

BELGIAN PATENT

filed by the company known as:

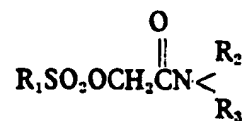
STAUFFER CHEMICAL COMPANY

for the following purpose: New herbicidal compounds and their use.

Qualification proposed: PATENT

(Handwritten) being the subject of a patent application, not yet granted to date, filed in the United States of America on September 13, 1963 in the name of Misters D.R. Baker, S.J.C. Soong and B.H. Lake

This invention relates to certain new compounds and their use as herbicides. More specifically, the present invention concerns new compounds having the structural formula:



in which R_1 is an alkyl, alkenyl, haloalkyl, haloalkenyl, phenyl or substituted phenyl group, in which the substituents may be halogen atoms, or alkyl or nitro groups; or is a thiophene, phenylalkyl or naphthyl group, and R_2 and R_3 which may be the same or different are hydrogen atoms or alkyl, alkenyl, cyclic alkyl, cyclic alkenyl, phenyl, phenylalkyl, furfuryl, alkoxyalkyl or cyclic alkyl ether groups. By "cyclic alkyl" or "cyclic alkenyl" as used herein is meant both a radical such as cyclohexyl which may be attached at the R_2 and/or R_3 position and, a radical such as hexamethylene which is attached at both the R_2 and R_3 positions and together with the adjacent N atom forms a heterocyclic ring system. It is understood that "cyclic alkyl ether groups" are groups in which the alkyl portions of the ether are attached to the nitrogen atom at the R_2 and R_3 positions so as to form a ring structure with the nitrogen atom.

The new compounds of the present invention may be prepared by reacting together the appropriately substituted glycolamide and the appropriate sulfonyl chloride in the presence of an organic base such as triethylamine.

As typical examples of synthesis, the following may be mentioned. However, these examples do not limit the invention in any way.

EXAMPLE 1: O-benzenesulfonyl-N-isopropyl glycolamide.

To the benzene (100 ml.) solution of N-isopropyl glycolamide (11.7 g., 0.10 moles) and benzene sulfonyl chloride (12.7 ml., 0.10 moles) was added 15.2 ml. of triethylamine at 15—20° C. over a period of five minutes while stirring. The mixture was stirred for one hour at 20-32° C. The mixture was washed with water (100 ml.), dilute hydrochloric acid (100 ml.), and water and then dried over magnesium sulfate and evaporated by suction to yield 22 g. of a light yellow liquid. Upon standing, the liquid crystallized. The product was recrystallized using n-butyl ether, washed with n-butyl ether and cyclohexane to yield 13.5 g. of crystals, m.p. 64-66° C.

EXAMPLE 2: O-methanesulfonyl-N-n-butyl glycolamide.

To the benzene (100 ml.) solution of N-n-butyl glycolamide (13.1 g., 0.10 moles) and methanesulfonyl chloride (7.7 ml., 0.10 moles) triethylamine was added (14 ml., 0.10 moles) at 16-23° C. over a period of twenty minutes while stirring and cooling. The mixture was stirred for one hour at 20-32° C. The mixture was washed with water (100 ml.), dilute hydrochloric acid (100 ml.), and water and then dried over magnesium sulfate. Evaporation by suction yielded 17 g. of an oil which formed crystals when scraped. The product was recrystallized in a cyclohexane mixture: ether and washed with a 50:50 mixture of ether and carbon tetrachloride to yield 8 g. of a first fraction (m.p. 54-56° C.) and 1 g. of a second fraction (m.p. 52-53° C.).

Analysis: Found: Sulfur 15.5%

Calculated: Sulfur 15.4%

EXAMPLE 3 - O-p-bromobenzenesulfonyl-N-n-butyl glycolamide.

To the benzene (100 ml.) solution of N-n-butyl glycolamide (6.5 g., 0.05 moles) and p-bromobenzenesulfonyl chloride (12.3 g., 0.05 moles) triethylamine (7 ml., 0.05 moles) was added at 13° C. Temperature is maintained at 13 - 20°C while stirring and cooling until the heat release ends and then is stirred for 1.5 hour at 20-25°C.

The mixture is washed with water (100 ml), dilute hydrochloric acid (100 ml) and water. It is then dried on magnesium sulfate and evaporated by suction which produces a light yellow oil that quickly crystallizes resulting in a crystalline mass. This was recrystallized in 75 ml. of n-butyl ether to yield 13 g. of product, m.p. 76-77° C.

Analysis: Found: Bromine 22.5%, Sulfur 8.98%

Calculated: Bromine 22.8%, Sulfur 9.15%

EXAMPLE 4 - O-methanesulfonyl N,N-di-n-propyl glycolamide

To the ether (100 ml.) solution of the N,N-di-n-propyl glycolamide (15.9 g., 0.10 moles) methane sulfonyl chloride (7.7 ml, 0.10 moles) triethylamine (14 ml., 0.10 moles) was added at 15-18° C, over a period of 45 minutes while stirring and cooling. The mixture was stirred for 40 minutes and is then washed with water (50 ml), dilute hydrochloric acid (50 ml) and water (50 ml). The etherized solution is dried on magnesium sulfate and evaporated by suction at 80°C (20 mm) to yield 19.5 g of a light yellow oil. Cooling with dry ice induced the formation of crystals. The crystals were washed with n-butyl ether and cyclohexane to yield 13 g. of crystals m.p. 35-37° C.

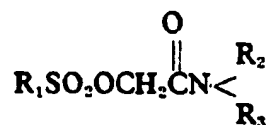
Analysis: Found: Sulfur 13.5%
Calculated: Sulfur 13.5%

The new compounds of the present invention have also been found to possess extremely interesting herbicidal properties.

The herbicidal activity of the compounds in accordance with the present invention was demonstrated by the following test.

Seven weed species were indiscriminately selected for testing each compound from the following group of weeds: *Digitalis* sp., *Echinochloa* sp., *Alopecurus* sp., *Avena fatua*, *Chenopodium album*, *Gyrotheca tinctoria*, *Amaranthus* sp., *Datura stramonium*, *Convolvulus arvensis*, *Avena striata*, *Brassica*, *Poa annua*, *Rumex* sp. and *Brassica juncea*. Seeds of the seven selected weed species are planted in individual rows 1.27 cm deep in Santa Cruz sandy loam soil contained in compressed paper flats measuring 20.95 by 16.51 cm with a depth of 6.93 cm. Enough weed seeds are planted to give about 30 to 50 plants of each of the selected weed species in each flat. The flats are watered after planting and the following day each flat is sprayed at a rate of 9072 g of the compound under test in 302.6 liters of solution per 0.4 hectare. A No. 152 DeVilbiss atomizer is used to spray the solution on the soil surface. Two weeks later, the degree of weed control is determined by comparing the amount of germination and growth of each weed in the treated flats with the weeds in several untreated control flats. In the results given below, the herbicidal effect of each compound with regard to each weed species is given separately and numbered from 1 to 3 (0—no control, 1—partial control, 2 good control, 3—complete control). The sum of these ratings based on the seven weed species employed

is then called the Activity Index (A.I.) and is indicated in the following Table:



Compound	R ₁	R ₂	R ₃	Activity Index
1	p-methylphenyl	hydrogen	i-propyl	20
2	phenyl	hydrogen	n-butyl	20
3	phenyl	hydrogen	i-propyl	20
4	methyl	hydrogen	n-butyl	18
5	p-bromophenyl	hydrogen	n-butyl	15
6	methyl	hydrogen	i-butyl	16
7	phenyl	ethyl	ethyl	21
8	methyl	ethyl	ethyl	21
9	p-bromophenyl	ethyl	ethyl	17
10	3,4-dichlorophenyl	hydrogen	i-propyl	11
11	ethyl	hydrogen	n-butyl	11
12	methyl	allyl	allyl	20
13	3,4-dichlorophenyl	allyl	allyl	18
14	3,4-dichlorophenyl	hydrogen	n-propyl	16
15	methyl	n-propyl	n-propyl	21
16	p-chlorophenyl	n-propyl	n-propyl	17
17	p-bromophenyl	n-butyl	n-butyl	9
18	methyl	— hexamethylene —		18
19	p-chlorophenyl	— hexamethylene —		15
20	phenyl	— hexamethylene —		17
21	methyl	— 2-Methyl-pentamethylene —		21
22	methyl	— pentamethylene —		20
23	benzyl	— hexamethylene —		20
24	benzyl	— pentamethylene —		18
25	p-nitrophenyl	n-propyl	n-propyl	10

Table (continued)

Compound	R ₁	R ₂	R ₃	Activity Index
26	naphthyl	allyl	allyl	12
27	p-nitrophenyl	— hexamethylene —		14
28	p-fluorophenyl	— hexamethylene —		19
29	methyl	i-butyl	i-butyl	6
30	p-methylphenyl	— hexamethylene —		20
31	methyl	hydrogen	cyclohexyl	17
32	p-chlorophenyl	hydrogen	i-butyl	18
33	p-nitrophenyl	hydrogen	i-butyl	14
34	p-nitrophenyl	hydrogen	i-propyl	12
35	p-chlorophenyl	hydrogen	cyclohexyl	9
36	p-nitrophenyl	hydrogen	cyclohexyl	6
37	CFCI ₂ CCl ₂ —	— hexamethylene —		16
38	methyl	methyl	methyl	12
39	methyl	— 3-oxa-pentylmethylene —		10
40	n-butyl	hydrogen	cyclohexyl	9
41	methyl	hydrogen	isopropoxypropyl	5
42	phenyl	hydrogen	isopropoxypropyl	12
43	CFCI ₂ CFCI—	allyl	allyl	5
44	phenyl	hydrogen	cyclohexyl	9
45	CH ₂ =CH—	hydrogen	cyclohexyl	8
46	methyl	— tetramethylene —		17
47	phenyl	— tetramethylene —		13
48	p-nitrophenyl	— tetramethylene —		13
49	ethyl	— hexamethylene —		15
50	ethyl	i-butyl	i-butyl	7
51	ethyl	hydrogen	cyclohexyl	13
52	n-butyl	hydrogen	3,4-dichlorophenyl	5
53	methyl	hydrogen	3,4-dichlorophenyl	5

Table (continued)

Compound	R ₁	R ₂	R ₃	Activity Index
54	CF ₂ ClCCl ₂ —	— hexamethylene —		14
55	m-nitrophenyl	— hexamethylene —		13
56	p-fluorophenyl	— pentamethylene —		9
57	3,4-dichlorophenyl	hydrogen	isopropoxypropyl	4
58	3,4-dichlorophenyl	— hexamethylene —		9
59	2-naphthyl	— hexamethylene —		16
60	p-iodophenyl	— hexamethylene —		13
61	3,4-dichlorophenyl	methyl	phenyl	7
62	methyl	methyl	phenyl	20
63	p-bromophenyl	— hexamethylene —		7
64	methyl	ethyl	n-butyl	19
65	ethyl	ethyl	n-butyl	21
66	n-butyl	ethyl	n-butyl	20
67	o-nitrophenyl	ethyl	n-butyl	14
68	p-fluorophenyl	ethyl	n-butyl	13
69	p-nitrophenyl	ethyl	n-butyl	12
70	p-chlorophenyl	ethyl	n-butyl	13
71	n-butyl	methyl	phenyl	16
72	p-chlorophenyl	methyl	phenyl	16
73	p-chlorophenyl	hydrogen	isopropoxypropyl	11
74	methyl	hydrogen	phenyl	9
75	ethyl	hydrogen	phenyl	6
76	butyl	hydrogen	phenyl	9
77	CHCl=CCl	— hexamethylene —		16
78	CH ₂ Cl—	— hexamethylene —		18
79	CH ₂ Cl—	ethyl	butyl	13
80	CH ₂ Cl—	hydrogen	cyclohexyl	7
81	methyl	hydrogen	allyl	19
82	o-thiophene	— hexamethylene —		20

Table (continued)

Compound	R ₁	R ₂	R ₃	Activity Index
83	o-thiophene	ethyl	butyl	16
84	methyl	— 4-methyl-pentamethylene —		21
85	butyl	— 4-methyl-pentamethylene —		20
86	methyl	— 3-methyl-pentamethylene —		20
87	butyl	— 3-methyl-pentamethylene —		17
88	CH ₂ Cl—	— 4-methyl-pentamethylene —		16
89	CH ₂ =CH—	— 4-methyl-pentamethylene —		20
90	phenyl	— 4-methyl-pentamethylene —		13
91	p-toluy	— 3-methyl-pentamethylene —		12
92	ethyl	— 3-methyl-pentamethylene —		17
93	p-toluy	— 3-methyl-pentamethylene —		18
94	ethyl	— 4-methyl-pentamethylene —		18
95	ethyl	— 3-methyl-pentamethylene —		21
96	methyl	methyl	butyl	20
97	ethyl	methyl	butyl	21
98	butyl	methyl	butyl	20
99	phenyl	methyl	butyl	19
100	ethyl	hydrogen	allyl	21
101	butyl	hydrogen	allyl	20
102	methyl	hydrogen	i-propyl	21
103	ethyl	hydrogen	i-propyl	21
104	methyl	hydrogen	ethyl	21
105	ethyl	hydrogen	ethyl	18
106	butyl	hydrogen	ethyl	21
107	butyl	hydrogen	i-propyl	21
108	phenyl	hydrogen	allyl	18
109	phenyl	hydrogen	ethyl	15
110	ethyl	— 2-methyl-pentamethylene —		18
111	butyl	— 2-methyl-pentamethylene —		19
112	methyl	hydrogen	methyl	7
113	ethyl	hydrogen	methyl	13

Table (continued)

Compound	R ₁	R ₂	R ₃	Activity Index
114	butyl	hydrogen	methyl	14
115	phenyl	hydrogen	methyl	15
116	methyl	hydrogen	propyl	21
117	ethyl	hydrogen	propyl	20
118	methyl	hydrogen	butyl	17
119	butyl	hydrogen	butyl	19
120	phenyl	hydrogen	propyl	15
121	phenyl	hydrogen	butyl	16
122	p-toluy	hydrogen	butyl	18
123	p-toluy	hydrogen	propyl	17
124	p-ethylphenyl	— hexamethylene —		17
125	4-dodecylphenyl	— hexamethylene —		16
126	phenyl	—2-methyl-pentamethylene—		16
127	p-toluy	— 2-methyl-pentamethylene —		18
128	methyl	ethyl	cyclohexyl	21
129	butyl	ethyl	cyclohexyl	12
130	ethyl	ethyl	cyclohexyl	18
131	phenyl	ethyl	cyclohexyl	13
132	methyl	— Δ^2 pentalene —		15
133	ethyl	— Δ^2 pentalene —		19
134	CH ₂ Cl—	— Δ^2 pentalene —		16
135	butyl	— Δ^2 pentalene —		21
136	methyl	ethyl	phenyl	19
137	ethyl	ethyl	phenyl	21
138	butyl	ethyl	phenyl	6
139	phenyl	ethyl	phenyl	5
140	propyl	— hexamethylene —		21
141	ethyl	allyl	allyl	21
142	butyl	allyl	allyl	21
143	phenyl	allyl	allyl	14
144	p-toluy	allyl	allyl	17

Table (continued)

Compound	R ₁	R ₂	R ₃	Activity Index
145	propyl	hydrogen	allyl	20
146	CH ₂ Cl—	hydrogen	allyl	21
147	propyl	— 2-methyl-pentamethylene —		21
148	propyl	— 3-methyl-pentamethylene —		21
149	ethyl	— pentamethylene —		21
150	butyl	— pentamethylene —		20
151	propyl	— pentamethylene —		21
152	phenyl	— pentamethylene —		10
153	methyl	hydrogen	i-butyl	16
154	butyl	hydrogen	i-butyl	20
155	propyl	hydrogen	i-butyl	21
156	phenyl	hydrogen	i-butyl	21
157	methyl	butyl	butyl	17
158	ethyl	butyl	butyl	16
159	ethyl	hydrogen	— CH ₂ CH ₂₀ (CH ₃) ₂	17
160	butyl	hydrogen	— CH ₂ CH ₂₀ (CH ₃) ₂	21
161	methyl	hydrogen	t-butyl	20
162	ethyl	hydrogen	t-butyl	21
163	propyl	hydrogen	t-butyl	17
164	butyl	hydrogen	t-butyl	20
165	phenyl	hydrogen	t-butyl	13
166	methyl	hydrogen	furfuryl	11
167	ethyl	hydrogen	furfuryl	15
168	propyl	hydrogen	furfuryl	19
169	butyl	hydrogen	furfuryl	13
170	phenyl	hydrogen	furfuryl	19
171	methyl	hydrogen	benzyl	6
172	ethyl	hydrogen	benzyl	8
173	propyl	hydrogen	benzyl	16
174	butyl	hydrogen	benzyl	18
175	phenyl	hydrogen	benzyl	14

Table (continued)

Compound	R ₁	R ₂	R ₃	Activity Index
176	methyl	— 2-ethyl-pentamethylene —		21
177	ethyl	— 2-ethyl-pentamethylene —		21
178	propyl	— 2-ethyl-pentamethylene —		21
179	butyl	— 2-ethyl-pentamethylene —		21
180	methyl	hydrogen	sec-butyl	21
181	ethyl	hydrogen	sec-butyl	20
182	propyl	hydrogen	sec-butyl	19
183	butyl	hydrogen	sec-butyl	18
184	phenyl	hydrogen	sec-butyl	18
185	ethyl	ethyl	ethyl	18
186	propyl	ethyl	ethyl	20
187	methyl	— 3,5-dimethyl-4-oxopentamethylene		18
188	ethyl	— 3,5 dimethyl-4-oxopentamethylene		18
189	propyl	— 3,5-dimethyl-4-oxopentamethylene		19
190	butyl	— 3,5-dimethyl-4-oxopentamethylene		19
191	phenyl	— 3,5-dimethyl-4-oxopentamethylene		18
192	benzyl	hydrogen	allyl	21
193	benzyl	allyl	allyl	21
194	benzyl	hydrogen	propyl	21
195	benzyl	hydrogen	i-propyl	21
196	benzyl	phenyl	ethyl	12
197	benzyl	hydrogen	i-butyl	20
198	benzyl	hydrogen	benzyl	13
199	benzyl	— 2-methyl-pentamethylene—		21
200	benzyl	— 3-methyl-pentamethylene —		21
201	benzyl	— 4-methyl-pentamethylene —		21
202	hexyl	— 2-methyl-pentamethylene —		16
203	octyl	— 2 methyl-pentamethylene —		12

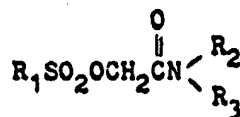
Table (continued)

Compound	R ₁	R ₂	R ₃	Activity Index
204	hexyl	hydrogen	i-propyl	18
205	octyl	hydrogen	i-propyl	12
206	hexyl	hydrogen	sec-butyl	16
207	hexyl	— 4-methyl-pentamethylene —		14
208	octyl	— 4-methyl-pentamethylene —		12
209	hexyl	— hexamethylene —		19
210	hexyl	allyl	allyl	16

In addition to the pre-emergence herbicidal activity indicated by the above table, the compounds in accordance with the present invention also exhibited excellent post-emergence herbicidal activity.

CLAIMS.

1.- Compounds of the following formula:



in which R₁ is an alkyl, alkenyl, haloalkyl, haloalkenyl, phenyl or substituted phenyl group, in which the substituents may be halogen atoms, or alkyl or nitro groups; or is a thiophene, phenylalkyl or naphthyl group, and R₂ and R₃ which may be the same or different are hydrogen atoms or alkyl, alkenyl, cyclic alkyl, cyclic alkenyl, phenyl, phenylalkyl, furfuryl, alkoxyalkyl or cyclic alkyl ether groups.

2.- The method of controlling the growth of weeds, characterized by the application to a weed habitat of a phytotoxic amount of a compound as claimed in claim 1.

Brussels, February 25, 1965
Stauffer Chemical
Company
(Illegible) HAEGHEN



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